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[71]申请人 富士电机株式会社

地址 日本神奈川县

[72]发明人 川田纪右 引间清

[74]专利代理机构 中国国际贸易促进委员会专利商
标事务所

代理人 全 菁

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[54]发明名称 电子照相用有机感光体及圆筒状支持体的
制造方法

[57]摘要

本发明涉及具有重量轻、生产率高、耐药品性及耐热性优良,即使是薄壁、细长形状也具有良好的尺寸精度,均匀的表面粗糙度,表面品质稳定而且密合性优良的圆筒状支持体的有机感光体。它是将以交联型 PPS 树脂作为主成分,其中配合有高导电性的炭黑(体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下)使其体积电阻率为 $10^4\Omega \cdot \text{cm}$ 以下的材料,经注射成型制成的圆筒状支持体上,涂覆有机材料形成的感光层而制得的感光体。

权 利 要 求 书

1. 电子照相用有机感光体, 其特征在于, 在以交联型聚亚苯基硫醚树脂为主成分, 其中还配合有体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑使其体积电阻率为 $10^4\Omega \cdot \text{cm}$ 以下的材料构成的圆筒状支持体上, 具备有机感光层。

2. 根据权利要求1所述的电子照相用有机感光体, 其特征在于, 在所述感光体中, 圆筒状支持体含有碳黑的平均粒度为 20nm 至 50nm 。

3. 根据权利要求1或2所述的电子照相用有机感光体, 其特征在于, 在所述感光体中, 圆筒状支持体含有碳黑的分散剂。

4. 根据权利要求3所述的电子照相用有机感光体, 其特征在于, 在所述感光体中, 分散剂是碳酸钙或粘土。

5. 根据权利要求1—4中任一项所述的电子照相用有机感光体, 其特征在于, 在所述感光体中, 圆筒状支持体含有作为增强材料的玻璃纤维。

6. 根据权利要求1—5中任一项所述的电子照相用有机感光体, 其特征在于, 在所述感光体中, 圆筒状支持体的交联型聚亚苯基硫醚树脂的量至少为 40 重量%以上。

7. 根据权利要求1—6中任一项所述的电子照相用有机感光

体,其特征在于,在所述感光体中,圆筒状支持体的表面用波长 180nm 至 255nm 的紫外线进行照射处理。

8. 根据权利要求 1—6 中任一项所述的电子照相用有机感光体,其特征在于,在所述感光体中,圆筒状支持体的表面经过电晕放电处理。

9. 根据权利要求 1—8 中任一项所述的电子照相用有机感光体,其特征在于,在所述感光体中,圆筒状支持体的壁厚为 3mm 以下。

10. 圆筒状支持体的制造方法,其特征在于,将以交联型聚亚苯基硫醚树脂为主成分,并在其中配合有体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑使其体积电阻率在 $10^4\Omega \cdot \text{cm}$ 以下的材料,用圆筒状支持体的金属模型注射成形。

11. 根据权利要求 10 所述的圆筒支持体的制造方法,其特征在于,在该方法中,用于注射成形的金属模型温度在 120°C 至 150°C 的范围内。

12. 根据权利要求 10 或 11 所述的圆筒支持体的制造方法,其特征在于,在该方法中,注射成形时的材料充填时间在 0.05 秒至 2.5 秒的范围内。

13. 根据权利要求 10—12 中任一项所述的圆筒支持体的制造方法,其特征在于,在该方法中,使用了具有:金属模型的芯模加工成其表面粗糙度的最大高度 R_{max} 为 $1\mu\text{m}$ 以下,且一侧面

具有 0.15° 至 0.25° 范围内的拔模斜度；阴模的内面没有拔模斜度，但施以镍合金的电铸加工使其表面粗糙度加工成最大 R_{max} 为 $1\mu m$ 以下，与固定模相接的端面内侧上形成台阶高差部位，通过该台阶高差部位以侧开口方式充填成形材料的结构；固定模与阴模相接的端面上，在阴模的圆周方向至少三等份划分的各处设置弹簧敲打器，在成形后开模时，已注射成形的成形品借助于该弹簧敲打器的作用必定保留在空腔侧的结构，作为特长的金属模型。

说 明 书

电子照相用有机感光体及 圆筒状支持体的制造方法

本发明涉及电子照相用有机感光体,更详细地说,涉及其导电性的圆筒状支持体,并涉及该圆筒状支持体的制造方法。

应用电子照相技术的复印机和打印机等的电子照相装置中使用的电子照相用有机感光体,是由导电性的支持体和含有设在其上的有机光导电性材料的有机材料组成的感光层构成。导电性支持体,从有利于装置设计的观点来看,通常做成圆筒状,然后将感光层涂覆并形成于该圆筒的表面上。

作为圆筒状支持体的材料,以前是较轻型的材料,多半使用机械加工性优良的铝或铝合金。

在特公平2—17026号公报中公开了,较轻型的,耐药品性、耐热性也优良,即使在大气中也不会因氧化而变质,作为适于有机感光体的圆筒状支持体,采用以聚亚苯基硫醚(以下简称PPS树脂)作为主成分的材料,用注射成形法制得的支持体。

然而,由铝或铝合金构成的支持体,为了获得支持体所要求的严格尺寸精度(圆度 $\pm 50\mu\text{m}$ 以下,直径的尺寸精度 $\pm 40\mu\text{m}$ 以

下)和适宜的表面粗糙度(最大高度 R_{max} 为 $0.5\mu m-1.2\mu m$, 因而每个都需要进行高精度的机械加工, 而且每个都还必须进行凹坑加工以便嵌合用于旋转驱动感光体的突缘, 此外, 还有受大气中水分和氧的影响以致表面氧化、变质的问题, 必须采取防止在表面上形成阳极氧化皮膜等变质的措施, 有制造工时多, 制造成本高的问题。

由以 PPS 树脂作为主成分的材料构成的支持体中, 存在下述问题。也就是, PPS 树脂的体积电阻率通常高达 $10^{10}\Omega \cdot cm-10^{13}\Omega \cdot cm$, 因此, 例如要在 PPS 树脂中添加碳黑以提供导电性。近年来, 对图象品质、印字特性的市场要求更为严格, 但对于为了获得实用上必要程度的良好质量的图象或良好印字特性所必需的支持体的导电性进行调查后, 判明了必须将支持体的体积电阻率至少规定在 $10^4\Omega \cdot cm$ 以下, 如果在 $10^4\Omega \cdot cm$ 左右以上, 则感光体曝光时及消电时在支持体上的电荷不易消除以致残余电位变大, 得不到良好的图象、印字。碳黑的体积电阻率, 是称为通常导电性碳黑的炉碳时, 则为 $1\Omega \cdot cm-10\Omega \cdot cm$, 为了使支持体的体积电阻率在 $10^4\Omega \cdot cm$ 以下, 碳黑的添加量必须超过 20 重量%, 而一旦添加如此大量的碳黑则材料的粘度会变高, 产生难以注射成型的问题。特别是, 近来需要小径(外径 30mm 左右以下)、薄壁(壁厚 3mm 左右以下)、长尺寸(长度为数百 mm)形状的支持体, 而这种形状的支持体其注射成型是极困难的。而且还会产生支持体的机械

强度降低的不利情况。进而，越是薄壁、长尺寸的支持体，越难以保持精度，由以普通线性型 *PPS* 树脂为主成分的材料构成的支持体，在其上涂覆形成有机材料层的过程中，因涂液的溶剂、加热而产生的、通常情况下不成为问题的微小变形成了问题，难以得到支持体所要求的尺寸精度。而且，由于 *PPS* 树脂的良好的耐药剂性，在其上涂覆形成的有机材料层的粘附性差，导致在感光体使用时感光层容易产生剥离，因此还有实用寿命短的问题。

本发明，鉴于上述情况，提出以下五个目的：第一，提供具有重量轻且有适宜导电性，耐药品性及耐热性优良，即使是薄壁，细长形状也能保持良好的尺寸精度，即使在大气中也不产生氧化等变质而能保持稳定质量的圆筒状支持体的有机感光体；第二，进一步提供具有适宜精糙度的均匀表面粗糙度的圆筒状支持体的有机感光体；第三，进一步提供具有机械强度大，即使薄壁、细长形状也难以变形的圆筒状支持体的有机感光体；第四，进一步提供具有粘结性优良，可在其上涂覆形成粘结性优良的有机材料层的圆筒状支持体的有机感光体；第五，以高的生产率制造第一、第二、第三目的提出的那种圆筒状支持体，特别是薄壁、小径、细长形状的支持体的制造方法。

按照本发明，上述第一目的是通过制作使用由将交联型的 *PPS* 树脂作为主成分，其中配合体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑使其体积电阻率在 $10^4\Omega \cdot \text{cm}$ 以下的材料构成的圆

筒状支持体，并在其上设置有机感光层的感光体来解决。

上述第二目的，是通过将圆筒状支持体中所含的碳黑的平均粒径规定在 20nm 至 50nm 来解决。

如果在添加碳黑时，同时添加碳黑的分散剂，则可使支持体材料中均匀地含有碳黑。作为分散剂，可列举碳酸钙或粘土。

第三目的，是通过使圆筒状支持体中含有作为增强材料的玻璃纤维来解决。

如上所述，支持体材料是在交联型的 *PPS* 树脂中分别添加碳黑、碳黑分散剂、玻璃纤维等而形成的材料，而为了发挥交联型 *PPS* 树脂的特长，其树脂量至少为 40 重量%以上。

第四目的，是通过通过对圆筒状支持体的表面用波长 180nm 至 255nm 的紫外线进行照射处理，或进行电晕放电处理来解决。

第五目的，是通过将以交联型 *PPS* 树脂作为主成分、并在其中配合体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑使其体积电阻率为 $10^4\Omega \cdot \text{cm}$ 以下的材料，或进一步添加平均粒径为 20nm 至 50nm 的碳黑的材料，或进一步添加玻璃纤维的材料注射成形来解决。

用于注射成形的金属模型的温度规定在 120°C 至 150°C 范围内，成形材料温度最好规定在 280°C 至 330°C 范围内。材料的充填时间为 0.05 秒至 2.5 秒范围内。

适于使用有以下特长的金属模型，作为成型金属模型的结构

是，芯型表面粗糙度的最大高度 R_{max} ，精加工成 $1\mu m$ 以下，而且一侧面具有 0.15° 至 0.25° 范围内的拔模斜度；阴模的内面设有拔模斜度，但施用镍合金的电铸加工，使表面粗糙度的最大高度 R_{max} 为 $1\mu m$ 以下；与固定模接触的端面内侧上形成台阶高差部位，通过该台阶高差部位以侧开口（サイドゲート）方式将成形材料充填到型腔内；固定模型与阴模接触的端面上，在阴模的圆周方向至少三等份划分的各个位置上设置弹簧敲打器（スプリングハンク

）、开模时注射成形的成形品借助于这种弹簧敲打的作用必定残留在空腔侧。

表 1 示出，对交联型的 *PPS* 树脂和线性型的 *PPS* 树脂，使用各自的圆筒状成形品，以在丙酮、二氯甲烷、二氯乙烷中各自浸渍 24 小时后的质量变化（%）评价的耐药品性以及用 $120^\circ C$ 加热 48 小时后直径方向、长度方向的尺寸变化（%）评价的耐热性。

表 1.

特性项目	线性型 P P S 树脂	交联型 P P S 树脂
耐药品性 (浸渍 2 4 小时后的 质量变化 (%))		
丙酮	+ 0.05	0
二氯甲烷	+12.42	+ 0.13
二氯乙烷	+ 3.40	0
耐热性 (1 2 0 ° C 加热 4 8 小时后的尺寸变化 (%))		
直径方向	- 0.67	- 0 .01
长度方向	- 1.20	0

从表 1 可清楚地看出, 交联型 *PPS* 树脂的耐药品性、耐热性都比线性型 *PPS* 树脂优良。由于采用以交联型 *PPS* 树脂为主成分的材料形成支持体, 因而支持体的热变形以及在涂覆形成由感光层等有机材料构成的膜层时因涂液溶剂导致的膨润较少, 故使支持体的变形降低, 即使是使用壁薄、小径、细长形的支持体, 也可获得实用上充分的尺寸精度。

为了给这种以交联型 *PPS* 树脂为主成分的材料以导电性而添加的碳黑, 被规定为其体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑, 例如高导电性的炉碳, 或较高导电性的槽法碳黑, 故可以使为了将支持体的体积电阻率达到要求的 $10^4\Omega \cdot \text{cm}$ 以下而添加的碳黑量至少为 20 重量%以下, 并且即使是小径、薄壁、细长形状也可以将支持体材料的粘度保持在可注射成形的范围内, 例如将温度 300°C 时的熔体流动率(*MFR*)保持在 20g/分钟—50g/分钟。

当然, 希望碳黑在支持体材料内尽可能地均匀分散。为此, 希望添加分散剂, 作为分散剂, 可列举碳酸钙、粘土。分散剂的添加量取决于碳黑的添加量, 为支持体材料的 10 重量%—30 重量%。不足 10 重量%时, 效果小; 如果超过 30 重量%, 则对材料的导电性等造成不好影响故不希望如此。

支持体的表面粗糙度取决于成形金属模型的阴模内面的表面粗糙度, 但也受添加在材料中的碳黑粒径的影响。由于将碳黑的

平均粒径规定在 20nm 至 50nm ，故可以将支持体的表面粗糙度的 R_{max} 保持在 $0.5\mu\text{m}$ — $1.2\mu\text{m}$ 范围内。

还由于在支持体材料中添加了玻璃纤维，弥补了因添加碳黑而造成的机械强度降低，可以得到壁厚 1mm 左右的支持体所需要的 $0.49 \times 10^8 \text{N/m}^2$ 以上的强度。玻璃纤维优选直径为 $20\mu\text{m}$ 左右，长为 3mm 左右的。玻璃纤维的添加量取决于碳黑的添加量，但规定为支持体材料的 10 重量%—30 重量%。不足 10 重量%时效果小，如果超过 30 重量%则对材料的导电性、支持体的表面粗糙度有坏影响，故而是有利的。

如上所述，支持体材料是在交联型的 *PPS* 树脂中添加碳黑、碳黑分散剂、玻璃纤维等的材料，但由于树脂的添加量为至少 40 重量%以上，这样就可以不损害交联型的 *PPS* 树脂的特长，按情况灵活运用。

PPS 树脂有粘合性差的缺点。作为工程塑料使用 *PPS* 树脂的电器和汽车有关领域中，为了改良它而进行紫外线照射或电晕放电使表面改性，从而提高粘合性的方法是已知的(日本接着学会 31 回年次大会(1993 年 6 月)：*PPS* 接着性的改良、日本接着学会志 Vol. 29, No. 4(1993)：紫外线的表面改性)。不过，作为感光体的支持体中的那种功能性材料，使用交联型 *PPS* 树脂的情况下，这些方法是否不会妨碍作为其支持体的功能而有效尚未搞清楚。本发明者们发现，通过使用波长 180nm — 255nm 的紫外线照射，借助紫

外线的能量由大气中的氧生成臭氧从而切断交联型 *PPS* 树脂的最表面的分子链，再加上大气中水分等的作用，生成—OH 基，—COOH 基等，使表面活性化，无损于作为支持体所需要的功能就可以大大地改善表面的可润湿性并提高其粘合性。电晕放电处理的情况下，借助电晕放电能量生成臭氧，可以获得与紫外线照射时同样的效果。

本发明的感光体用支持体，是将以交联型的 *PPS* 树脂作为主成分，在其中添加碳黑，进而添加碳黑分散剂和玻璃纤维的材料并注射成形而制成。将用于成形的金属模型做成适宜的结构，在适宜的成形条件下整体成形，因而可以按照满意的尺寸精度、高的生产率制得具有规定形状、表面粗糙度的支持体。不必像用铝合金制造支持体那样，每个都要进行机械加工、表面粗糙度加工。如果将用于注射成形的金属模型的温度规定在 120℃—150℃ 的范围内，成形材料的温度规定在 280℃—330℃ 的范围内，施加足够的注射压力，将材料的充填时间规定在 0.05 秒—2.5 秒的范围内，即使是 3mm 以下的薄壁、长度为数百 mm 的细长形支持体注射成形时，在空腔(材料充填部分)内树脂开始固化前就可以完全结束材料的充填从而获得良好形状的支持体，而且，树脂的结晶化可充分进行从而发挥交联型 *PPS* 树脂的特性。

以下，对用于制造本发明支持体的成形金属模型，参照附图说明其作用。图 3—图 5 是说明本发明的成形用金属模型的一个实

施例的部分剖面图，图 3 示出阴模 6 的端面和固定模 8 的端面密合时的合模状态，7 是芯模，9 是充填成形材料并形成成形品的空腔。图 4 示出成形后的阴模 6 和固定模 8 脱离和开模时的状态，14 是成形品。芯模 7 嵌入固定模 8 内固定起来。图 5 是图 3 的弹簧敲打器 11 及其周围部分的放大剖面图。12 是弹簧，13 是敲击头。

阴模 6 与固定模 8 相接的端面内侧上形成台阶高差部位 10。台阶高差部位 10 的尺寸，可以是将图 5 中示出的台阶高差部位 10 的 h 规定为 $1\text{mm}—3\text{mm}$ ， W 规定为 $2\text{mm}—5\text{mm}$ 。图 3 的合模状态下，通过该台阶高差部位 10 以侧开口方式将成形材料充填到空腔 9 内，于是，成形材料首先填满台阶高差部位 10 后再充填薄壁圆筒柱的空腔 9，这就可以沿圆周方向均匀而且迅速地、不产生缝隙等缺陷地一直充填到空腔 9 的前端。为了能以 0.05 秒—2.5 秒的高速充填材料，在空腔 9 的前端部位设有通气口，进一步还可根据需要做成可真空排气的结构。此外，阴模 6 的内面，为了复制性、脱模性优良，施以镍合金的电铸加工，使其表面粗糙度的最大高度 R_{\max} 为 $1\mu\text{m}$ 以下。使用有如此表面状态的阴模 6，以足够的注射压力将充填材料充填到空腔 9 中并固化。就可以使注射成形得到的支持体的表面具有最大高度 R_{\max} 为 $1\mu\text{m}$ 以下的粗糙度。

然而，作为感光体，要求外径相同，因此不允许在成形品的外径上有拔模斜度。这样的成形品，特别是不损害表面地将薄壁成形品从阴模 6 上脱模是极为困难的。因此，要将芯模 7 的表面精加工

成表面粗糙度的最大高度 R_{max} 为 $1\mu m$ 以下的光滑表面,而且具有一侧面为 0.15° 至 0.25° 范围内的拔模斜度,进而,在固定模 8 的端面与阴模 6 相接的部位,在阴模 6 的圆周方向至少三等分划分的各位置上设置由敲击头 13 和弹簧 12 构成的弹簧敲打器 11。由于采用了这种构造,合模时如图 5 所示压缩着的弹簧 12 在开模时伸开,以致敲击头 13 的前端如图 4 所示从固定模 8 端面顶出。敲击头 13 的前端顶出的长度,相当于图 5 所示 m 的长度。因此,在成形后阴模 6 脱离固定模 8 的过程中,敲击头 13 的前端继续推压阴模 6 和成形品 14 直至两个模按照相当于 m 的长度的距离分开,因而阴模 6 和成形品 14 成整体地移动,开模后如图 4 所示,成形品 14 与芯模 7 脱离后固定在阴模 6 一侧而保留下来。由于在芯模上形成拔模斜度,而且表面精加工成光滑状,因而开模时芯模顺利地与成形品 14 脱离。由于脱掉芯模 7,成形品 14 在直径方向上收缩,不会损伤表面就可以利用例如敲打方法从阴模 6 中取出成形品 14。芯模 7 的拔模斜度,在一侧面不足 0.15° 时芯模难以脱模;而如果拔模斜度超过 0.25° ,则发现作为成形品的支持体的壁厚为 $3mm$ 左右以下的薄壁情况下,其薄端的壁厚太薄而不能成形。例如,在一侧面的拔模斜度为 0.25° 情况下,外径 $30mm$ 、长 $300mm$,壁厚 $1.5mm-3mm$ 的支持体中,如果厚端的壁厚为 $1.5mm-3mm$,则薄端的壁厚就成为 $0.3mm-0.6mm$,成形极为困难。因此,拔模斜度,在一侧面中必须是在 $0.15^\circ-0.25^\circ$ 的范围

内。

图 6 是表示从金属模型中取出状态的成形品的斜视图，在圆筒状支持体 1 的一端，对应于阴模 6 的台阶高差部位 10 形成环状凸部 15，16 是侧开口。

图 1 是本发明感光体的支持体的一个实施例的模式断面，图 1(a)表示支持体 1 的纵断面图，图 1(b)是表示图 1(a)的 X—X 断面图。图 2 是表示感光体的一个实施例的层构成的模式断面图，在图 1 示出的支持体 1 上设置有通过底层 2 顺次层叠电荷发生层 4，电荷输送层 5 的感光层 3。底层 2 是根据需要设置，不一定是必需的。

实施例 1

用表 2 中示出的配合材料 1—1~1—4，使用图 3—图 5 中示出的金属模型，如表 3 所示，支持体 No. 1—支持体 No. 3 以同一成形条件，使用材料的树脂是线性型 PPS 树脂的材料 1—4 的支持体 No. 4，是通过改变金属模型温度，注射成形出具有外径为 30mm，长度为 260.5mm，内径在薄壁端为 28.5mm，在厚壁端为 26.5mm 那样拔模斜度的支持体 1—1~1—4。

表 2

原材料	原材料牌号	配合比(重量%)			
		材料 1-1	材料 1-2	材料 1-3	材料 1-4
交联型 P P S 树脂	東レ PPS M2900 (MFR:600)	60	-	-	-
	東レ PPS M 3910 (MFR:2000)	-	50	50	-
线性型 P P S 树脂		-	-	-	50
碳 黑	キャボット 炉碳黑 XC12 (粒径 30 nm)	15	-	-	-
	キャボット 炉碳黑 BP-480 (粒径 30 nm)	-	20	10	20
粘 土	土屋高岭土 SATINTONES	10	15	25	15
玻璃纤维	日本板硝子 RES 03-TP75 (直径约 20 μ m, 长度约 3 mm)	15	15	15	15

表 3

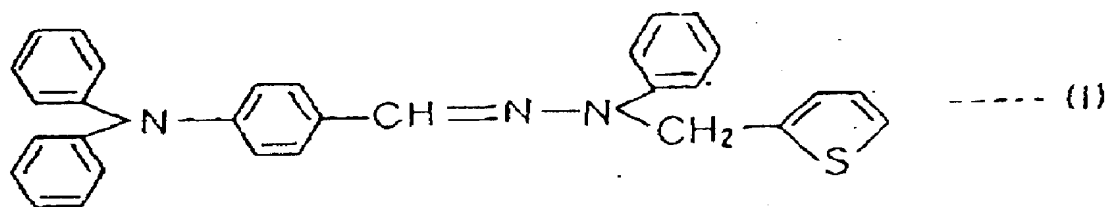
支持体号	1-1	1-2	1-3	1-4
支持体的材料	材料 1 - 1	材料 1 - 2	材料 1 - 3	材料 1 - 4
圓筒体温度 (°C)		(同左)	(同左)	
后部	280			280
中部	290			290
前部	300			300
喷嘴温度 (°C)	310			300
金属模型温度 (°C)	150			120
注射压力 ($\times 10^8 \text{ N/m}^2$)	1.62			1.62
充填时间 (sec)	0.1			0.1
冷却时间 (sec)	30			30

在这些支持体上，以同一条件形成下述感光层从而制成感光体。也就是，将醇可溶性聚酰胺树脂(东 I(株)制；アミラン CM8000)5 重量份 溶解于甲醇 95 重量份中的涂液用浸渍涂覆法涂覆，于温度 120℃ 下干燥 15 分钟后形成膜厚约 0.5 μ m 的底层。

用浸渍涂覆法在该底层上涂覆将 X 型无金属酞菁(大日本イソギ

化学工业(株)制；FASTGEN BLUE 8120) 10 重量份和氯乙烯系树脂(日本 ビボソ(株)制；MR-110) 10 重量份与二氯甲烷 686 重量份和 1,2-二氯乙烷 294 重量份一起用混合机混合分散 1 小时，进而用超声波分散机分散 30 分钟后制得的涂液，于温度 80℃ 干燥 30 分钟后形成膜厚约 0.5 μ m 的电荷发生层。在该电荷发生层上，用浸渍涂覆法涂覆由下述结构式(I)表示的腙化合物(富士电机(株)制)100 重量份，聚碳酸酯树脂(三菱瓦斯化学(株)制；

エーピロン POZ) 100 重量份、二氯甲烷 800 重量份组成的涂液，于温度 90℃ 干燥 1 小时后形成膜厚约 20 μ m 的电荷输送层，从而制得感光体。



对如此制得的各感光体，进行以下项目的评价：支持体材料的温度为 300°C 时的 MFR 、体积电阻率、注射成形性、机械强度、耐药品性（在二氯甲烷中浸渍 2 小时的质量变化率评价）、支持体的表面粗糙度（最大高度 R_{max} ）、外径尺寸精度、在温度 120°C 时进行 48 小时热处理后的尺寸变化率，及感光体在暗处带电后 5 秒放置后的电位保持率 V_{KS} ，将波长 780nm 的单色光经 $10\mu\text{J}/\text{cm}^2$ 照射后的残余电位 V_r ，实装在市售的半导体激光打印机上评价的印字特性，结果示于表 4 中。

表 4

感光体号	1-1	1-2	1-3	1-4
支持体号	1-1	1-2	1-3	1-4
MFR (g/10分)	30	40	30	40
体积电阻率 ($\Omega \cdot \text{cm}$)	2×10	3×10^2	10^6	3×10^2
注射成形性	良好	良好	良好	大致良好
机械强度 ($\times 10^8 \text{N/m}^2$)	0.68	0.68	0.74	0.78
耐药品性 (%)	+0.5	+0.1	+0.1	+12.4
表面粗糙度 R_{max} (μm)	0.9	0.8	0.8	0.8
外径尺寸精度 ($\pm \text{mm}$)	0.05	0.03	0.03	0.05
尺寸变化率 (%)	0	0	0	-0.7
V _{k5} (%)	90	92	93	92
V _r (v)	31	34	60	35
印字特性	良好	良好	印字不良	大致良好

从表 4 可清楚地看出,使用以线性型 *PPS* 树脂为主成分的材料 1—4 的支持体 1—4,与使用以交联型 *PPS* 树脂为主成分的材料 1—1、1—2、1—3 的支持体 1—1、1—2、1—3 相比较,其耐药品性差,尺寸变化率大。而且使用体积电阻率高为 $10^5 \Omega \cdot \text{cm}$ 的支持体 1—3 的感光体 1—3,其印字特性差。以交联型的 *PPS* 树脂作为主成分,由体积电阻率为 $10^4 \Omega \cdot \text{cm}$ 以下的材料构成的支持体的效果是很明显的。

实施例 2

对实施例 1 的支持体 1—1,使用 センエンジ=プリング(株)制的紫外线照射装置(型号:SUV200NS),将低压水银灯和支持体的间隔规定为 20mm,由 200W 的低压水银灯对支持体表面用波长 184.9nm 及 253.7nm 的紫外线照射。将照射时间为 10 秒的定为支持体 2—1,照射时间为 20 秒的定为支持体 2—2。

同样,使用支持体 1—1,一边使之旋转一边进行电晕放电(放电电压约 10KV,放电电极和支持体的间隙为 2mm—3mm,放电时间 30 秒),制成支持体 2—3。

为了进行比较,对同样的支持体 1—1 不施以电晕放电处理的,定为支持体 2—4。

用纯水来测定这些支持体的表面接触角,并进行粘着强度试验(JIS K5400 8.5.1),评价其粘合性。

然后，使用这些支持体按与实施例 1 相同方法制作感光体 2—1、2—2、2—3、2—4，安装在市售的半导体激光打印机上，连续复印直至感光层开始剥离而成问题，调查其连续复印寿命。

所得结果示于表 5 中。

表 5

感光体号	2-1	2-2	2-3	2-4
支持体号	2-1	2-2	2-3	2-4
表面处理				
紫外线照射(秒)	10	20	-	-
电晕放电(秒)	-	-	30	-
接触角(度)	32	0	0	78
粘着强度试验 (剥离/100)	85/100	0/100	0/100	100/100
连续复印寿命(次)	50,000	100,000	100,000	5,000

从表 5 中可清楚地看出,使用进行过紫外线照射的支持体 2—1、2—2 的感光体 2—1、2—2,及使用进行过电晕放电的支持体 2—3 的感光体 2—3,与使用不经过这些处理的支持体 2—4 的感光体 2—4 相比较,其粘着强度试验,连续复印寿命方面均较优良。照射 200W 低压水银灯的紫外线的情况下,以照射 20 秒的情况尤其优良,因而推定最好的照射时间为 15 秒—25 秒。

实施例 3

使用表 2 的材料 1—3,并采用图 3—图 5 的金属模型,如表 6 所示的成形条件中改变金属模型温度进行注射成形,从而制成支持体 3—1、3—2、3—3。当改变金属模型温度时,喷嘴温度也有若干改变。而且,对支持体 3—3 来说,由于提高了金属模型温度使材料的充填时间缩短了。在如此形成的支持体中,支持体 3—3 产生毛刺多,成形不良而不能作为支持体使用。继续用支持体 3—1、3—2,按与实施例 1 相同方法制作感光体 3—1、3—2,调查各自的 V_{KS} V_r 及印字特性。其结果示于表 7 中。

表 6

支持体号	3-1	3-2	3-3
圆筒体温度 (°C)			
后部	280	280	280
中部	290	290	290
前部	300	300	300
喷嘴温度 (°C)	310	300	319
金属模型温度 (°C)	150	100	170
注射压力 ($\times 10^8 \text{ N/m}^2$)	1.62	1.62	1.57
充填时间 (sec)	0.1	1.0	0.04
冷却时间 (sec)	30	30	30

表 7

感光体号	3-1	3-2
V k5 (%)	92	93
V r (V)	34	55
印字特性	良好	印字不良

从表 6、表 7 中可清楚地看出，即使是同一材料，但如果注射成形条件不适宜，也得不到良好的支持体，金属模型温度为 150℃ 时良好，而在 100℃ 时则印字不良，在 170℃ 时则产生毛刺等不良现象。作为金属温度，希望是 100℃ 以上—170℃ 以下，最好在约 120℃—160℃ 的范围内。

本发明，由于有以上说明的构成，因而可获得下述的效果。

由于使用了以交联型 *PPS* 树脂为主成分，其中还配合有体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下的高导电性碳黑使其体积电阻率为 $10^4\Omega \cdot \text{cm}$ 以下的材料构成的圆筒状支持体，因而可获得具有重量轻且有适宜导电性、耐药品性和耐热性优良、而且即使是薄壁、细长形状也能保持良好尺寸精度，即使在大气中也不会产生氧化等变质，因而不需要进行特殊表面稳定化处理的有机感光体。

由于将配合在支持体中的碳黑的平均粒径规定在 20nm 至 50nm，则可以获得具有表面粗糙度的 R_{max} 在 0.5 μm 至 1.2 μm 适宜范围内的均匀圆筒状支持体的有机感光体。由于在添加碳黑时还一起添加碳黑分散剂，因而可以均匀地添加碳黑，支持体呈均质，而且表面粗糙度也很均匀。

此外，还由于在支持体材料中添加玻璃纤维，则可以获得具有机械强度大，即使是薄壁、细长形状也难以变形的圆筒状支持体的有机感光体。玻璃纤维最好是直径为 20 μm 左右、长度为 3mm

左右,这种形状对支持体的粗糙度不会有坏影响。而且,即使如上所述有各种物质的添加,但如果交联型 *PPS* 树脂至少为支持体材料的 40 重量%以上,就能无任何损害地发挥其特长。

由于用波长 180nm — 255nm 的紫外线照射支持体的表面,或者对其表面进行电晕放电,因而可获得具有粘合性优良,可在其上形成密合性优良的有机材料层的圆筒状支持体并且使用寿命提高的有机感光体。

上述圆筒状支持体,由于是将以交联型 *PPS* 树脂作为主成分,其中配合有体积电阻率为 $10^{-1}\Omega \cdot \text{cm}$ 以下高导电性的碳黑使其体积电阻率为 $10^4\Omega \cdot \text{cm}$ 以下的材料,或进一步添加将碳黑粒径规定为 20nm 至 50nm 的材料,或还添加了玻璃纤维的材料注射成形,因而可以高的生产率制得。

注射成形时,如果金属模型温度在 120°C 至 150°C 范围内,成形材料温度在 280°C 至 330°C 范围内,则可成形为良好的上述成形材料,而且树脂的结晶化可充分进行,可得到能发挥交联型 *PPS* 树脂特性的支持体。而且,如果材料的充填时间在 0.05 秒至 2.5 秒范围内,则可形成良好的薄壁、细长形状的圆筒形支持体。关于成形用金属模型,采用具有以下特长的成形用金属模,即,嵌入固定模中的芯模其表面粗糙度加工成其最大高度 R_{\max} 为 $1\mu\text{m}$ 以下,而且一侧上具有 0.15° 至 0.25° 范围内的拔模斜度;阴模的内面没有拔模斜度,但施以镍合金的电铸加工使其表面粗糙度加工成最

大 R_{max} 为 $1\mu m$ 以下, 与固定模相接的端面内侧上形成台阶高差部位, 通过该台阶高差部位以侧开口方式充填成形材料的结构; 固定模与阴模相接的端面上, 在阴模的圆周方向至少三等份划分的各处设置弹簧敲打器, 在成形后开模时, 注射成形的成形品借助于该弹簧敲打器的作用必定保留在空腔侧的这种结构。由于采用这种结构的金属模型, 使成形材料的充填时间很容易加快成 0.05 秒至 2.5 秒, 在材料开始固化前就能将材料按圆周方向均匀地充分充填至空腔的前端, 从而能够良好地成形为薄壁、细长形状的支持体。而且, 相应于阴模内面的粗糙度, 可得到表面粗糙度的最大高度 R_{max} 为 $1\mu m$ 以下的支持体。注射成形后, 开模时因其芯模表面光滑而且有拔模斜度, 因而能顺利地将芯模从成形品中取出。其后, 可以将成形品从阴模中, 例如利用敲击, 将作为成形品的支持体, 表面无损伤地取出。

以下简单说明附图。

图 1 是本发明支持体的一个实施例的模式断面图, 图 1(a) 是纵断面图, 图 1(b) 是图 1(a) 的 X—X 断面图。

图 2 是本发明感光体的一个实施例的模式断面图。

图 3 是说明涉及本发明的金属模型的合模状态的部分断面图。

图 4 是说明涉及本发明的金属模型的开模状态的部分断面图。

图 5 是图 3 中弹簧敲打器部位及其周围部位的放大断面图。

图 6 是表示已从金属模型中取出状态的成形品的斜视图。

图中符号说明如下。

1. 支持体
2. 底层
3. 感光层
4. 电荷发生层
5. 电荷输送层
6. 阴模
7. 芯模
8. 固定模
9. 空腔
10. 台阶高差部位
11. 弹簧敲打器
12. 弹簧
13. 敲击头
14. 成形品
15. 环状凸部
16. 侧开口

图 1

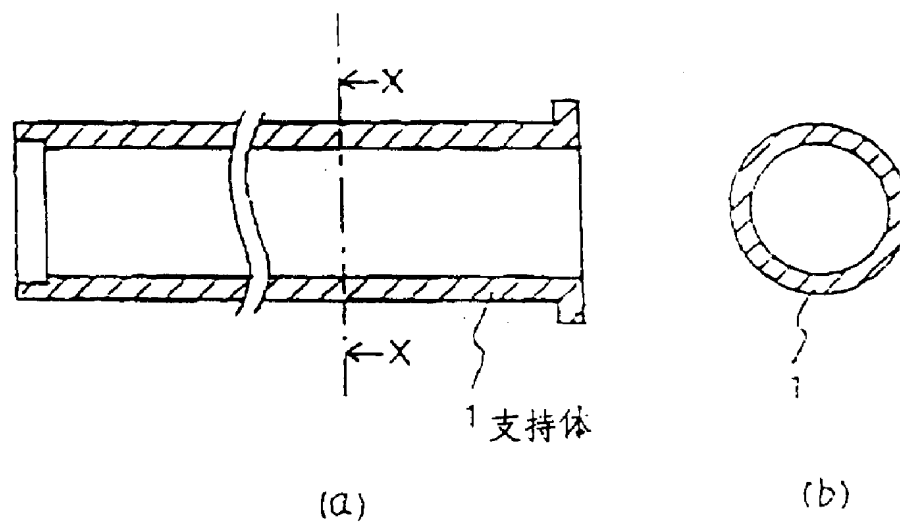


图 2

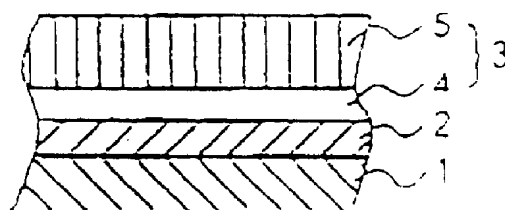


图 3

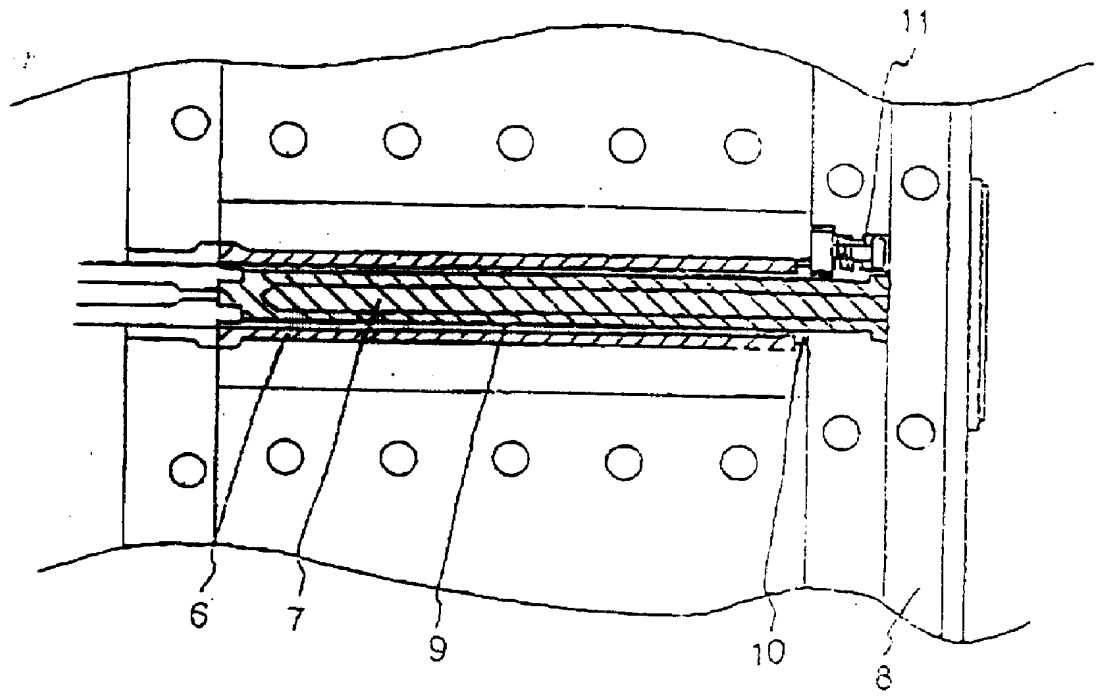


图 4

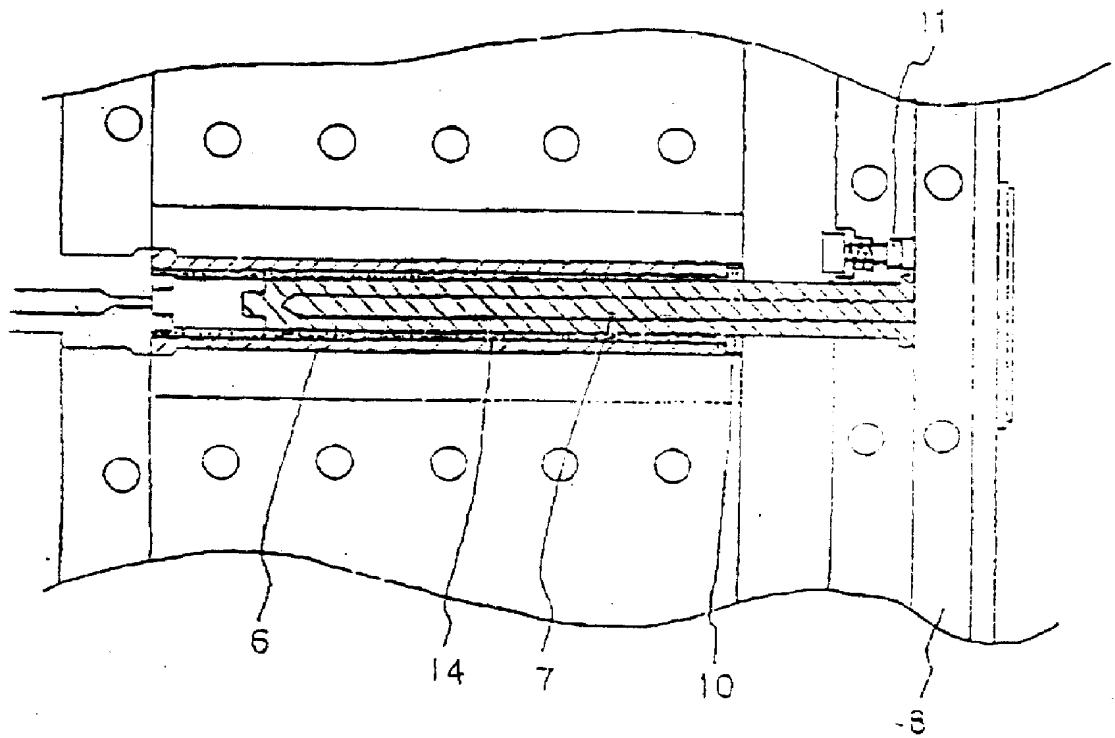


图 5

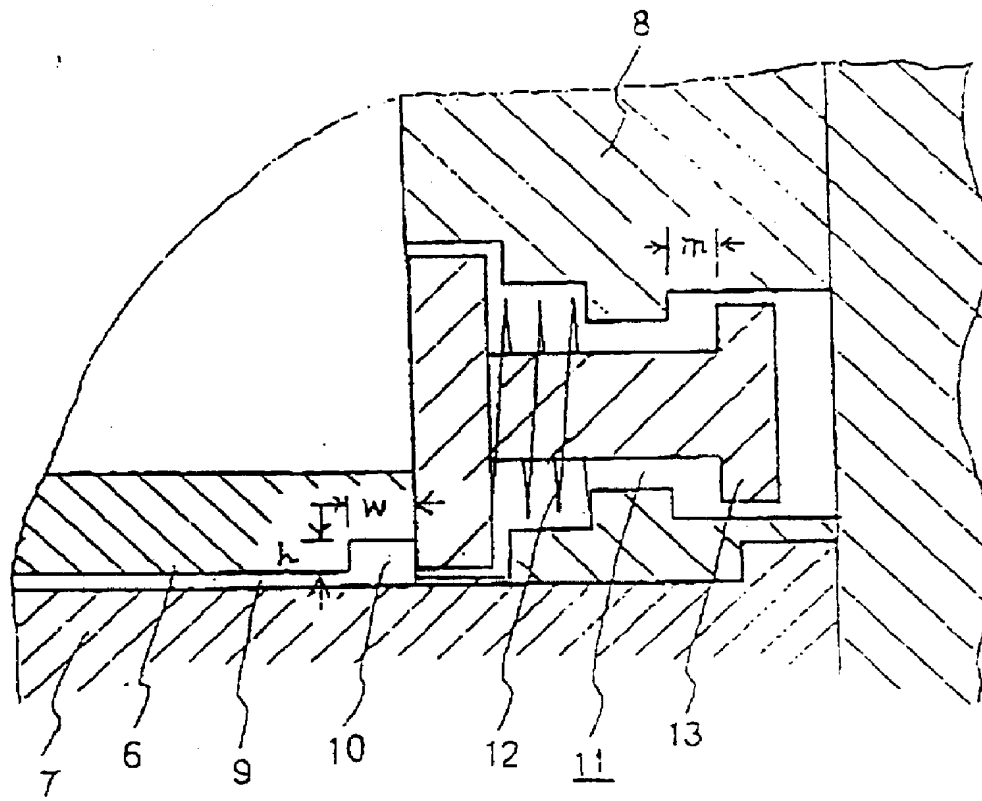
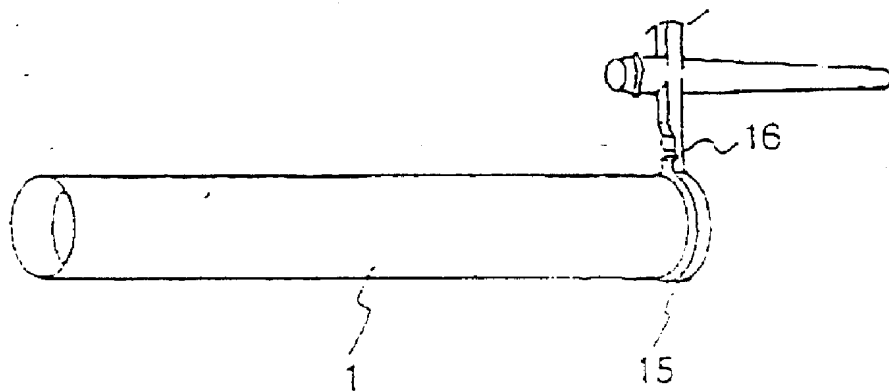


图 6



Translation of CN1119285A (Reference 1) by Jeekai & Partners

Chinese patent application No. 200480025104.2

Your Ref.: 089498.0454.CN

Our Ref.: Z0601027CPCN

Manufacturing method of organic photosensitive body and cylindrical supporting body for electrophotography**Abstract**

The invention relates to an organic photosensitive body with a cylindrical supporting body that has a light weight with good productivity and good chemical and thermal resistance, provides dimensional accuracy despite its thin and long shape, and also has a uniform surface roughness, stable surface quality, and good adhesion. The photosensitive body is provided by coating and forming a photosensitive layer of an organic material on a cylindrical supporting body formed by injection-molding a material $10^4 \Omega \cdot \text{cm}$ or less in volume resistivity formed by blending a crosslinked-type PPS resin as a main component with a highly conductive carbon black ($10^{-1} \Omega \cdot \text{cm}$ or less in volume resistivity).

What is claimed:

1. An organic photosensitive body for electrophotography, characterized in that the organic photosensitive body has an organic photosensitive layer on a cylindrical supporting body composed of a material of $10^4 \Omega \cdot \text{cm}$ or less in volume resistivity formed by blending a crosslinked-type polyphenylenesulfide resin as a main component with a highly conductive carbon black $10^{-1} \Omega \cdot \text{cm}$ or less in volume resistivity.
2. The organic photosensitive body for electrophotography of Claim 1, characterized in that in the photosensitive body, the average particle diameter of the carbon black contained in the cylindrical supporting body is 20 to 50 nm.
3. The organic photosensitive body for electrophotography of Claim 1 or 2, characterized in that in the photosensitive body, the cylindrical supporting body contains a carbon black dispersing agent.
4. The organic photosensitive body for electrophotography of Claim 3, characterized in that in the photosensitive body, the dispersing agent is a calcium carbonate or clay.

5. The organic photosensitive body for electrophotography of any of Claims 1 to 4, characterized in that in the photosensitive body, the cylindrical supporting body contains glass fibers as a reinforcement.
6. The organic photosensitive body for electrophotography of any of Claims 1 to 5, characterized in that in the photosensitive body, the amount of the crosslinked-type polyphenylenesulfide resin contained in the cylindrical supporting body is at least 40 wt.% or more.
7. The organic photosensitive body for electrophotography of any of Claims 1 to 6, characterized in that in the photosensitive body, the surface of the cylindrical supporting body is irradiated with ultraviolet rays of 180 to 255 nm in wavelength.
8. The organic photosensitive body for electrophotography of any of Claims 1 to 6, characterized in that in the photosensitive body, the surface of the cylindrical supporting body is treated with corona discharge.
9. The organic photosensitive body for electrophotography of any of Claims 1 to 8, characterized in that in the photosensitive body, the thickness of the cylindrical supporting body is 3 mm or less.
10. A manufacturing method of a cylindrical supporting body, characterized in that a material $10^4 \Omega \cdot \text{cm}$ or less in volume resistivity formed by blending a crosslinked-type polyphenylenesulfide resin as a main component with a highly conductive carbon black $10^{-1} \Omega \cdot \text{cm}$ or less in volume resistivity is injected into a metal mold for the cylindrical supporting body.
11. The manufacturing method of a cylindrical supporting body of Claim 10, characterized in that in the method, the metal mold for injection-molding is heated within a range of 120°C to 150°C .
12. The manufacturing method of a cylindrical supporting body of Claim 10 or 11, characterized in that in the method, filling time of an injection-molding material is within the range of 0.05 to 2.5 seconds.
13. The manufacturing method of a cylindrical supporting body of any of Claims 10 to 12, characterized in that in the method, a metal mold is used, wherein a core mold of the metal mold is finished to have a surface roughness of $1 \mu\text{m}$ or less at the maximum height R_{max} and a draft angle of 0.15° to 0.25° on one side; the inner surface of the cavity mold does not have a draft angle, is electroformed with a nickel alloy, finished to have a surface roughness of $1 \mu\text{m}$

or less at the maximum height R_{\max} , and has inside of the end face that contacts a fixed mold a stage section via which a material is filled using a side gate method; and the fixed mold is provided with at least three sprig knocks at its end face opposite to the circumference of the end face of the cavity mold to ensure that when the mold is opened, the injection-molded product remains in the cavity mold due to the effect of the spring knock.

Description

The present invention relates to an organic photosensitive body for electrophotography, and, in particular, to a conductive cylindrical supporting body therefor. This invention also relates to a manufacturing method of the conductive cylindrical supporting body.

A photosensitive body of electrophotography that is used for an electrophotography device such as a copier or printer to which electrophotography technology is applied comprises a conductive supporting body and a photosensitive layer provided thereon and consisting of an organic material containing an organic photoconductive material. The conductive supporting body is usually cylindrical for the convenience of the design of the device, and the photosensitive layer is coated and formed on its outer surface.

As materials for the cylindrical supporting body, aluminum or its alloy is conventionally used, especially that has a relatively light weight and a good machinability.

Japanese Patent Examined Publication No. 2-17026 discloses a supporting body manufactured by an injection-molding method using a material containing a polyphenylenesulfide resin (simply referred to as PPS below) as a main component, the supporting body that has a light weight and good chemical and thermal resistance, is not oxidized or otherwise deteriorated in the air, and is thus preferable for an organic photosensitive body.

However, supporting bodies composed of aluminium or its alloy require individual high accuracy machining to obtain a rigid dimensional accuracy ($\pm 50 \mu\text{m}$ or less in roundness and $\pm 40 \mu\text{m}$ in the accuracy of diameter) and a preferable surface roughness ($0.5 \mu\text{m}$ to $1.2 \mu\text{m}$ at the max. height R_{\max}) and also require individual machining of a spigot into which a flange for rotatably driving a photosensitive body is fitted; have a disadvantage that the surface is oxidized or deteriorated due to the effect of moisture or oxygen in the air; require to prevent deterioration, for example, by forming an anodic oxidized coat on the surface; and thus require many steps and costs in manufacturing process.

Supporting bodies composed of PPS resin as a main component have the following disadvantages. Since the volume resistivity of a PPS resin is high, that is, usually $10^{10} \Omega\cdot\text{cm}$ to $10^{13} \Omega\cdot\text{cm}$, a carbon black is added to the PPS resin to provide conductivity. The market has recently been making demands on image quality and printing characteristics. Investigations into the conductivity of supporting bodies required to obtain as good image quality and printing characteristics as required in practical use, have revealed that the volume resistivity should be $10^{-4} \Omega\cdot\text{cm}$ or less and that a higher volume resistivity than $10^{-4} \Omega\cdot\text{cm}$ prevents the removal of electric charges from the supporting body when the photosensitive body is exposed or static electricity is eliminated from the photosensitive body, resulting in an increase in residual potential, thereby preventing good images or printed characters from being obtained. The volume resistivity of a furnace carbon, which is usually used as a conductive carbon black, is 1 to $10 \Omega\cdot\text{cm}$, and more than 20 wt.% carbon black must be added to provide the supporting body with a volume resistivity of $10^{-4} \Omega\cdot\text{cm}$. However, addition of such a large quantity of carbon black increases the viscosity of the material, making injection-molding difficult. Supporting bodies of a small diameter (about 30 mm or less in outer diameter), a small thickness (about 3 mm or less), and a large length (several hundred mm) which have recently been demanded are very difficult to be made by injection-molding. In addition, such supporting bodies have a reduced mechanical strength. Moreover, thinner and longer supporting bodies with dimensional accuracy are more difficult to provide. Supporting bodies composed of an ordinary linear-type PPS resin as a main component are affected by a slight deformation that is caused by a solution of coating liquid or heating during coating and formation of an organic material layer on the supporting body, making the dimensional accuracy required for the supporting body difficult to obtain. In addition, the good chemical resistance of PPS resins prevents the adhesion of an organic material layer to the surface of the resin during coating and formation, causing frequent release of the photosensitive layer during the use of the photosensitive body, thereby resulting in a short effective life.

In view of the above points, the present invention provides five objects. It is a first object of this invention to provide an organic photosensitive body with a cylindrical supporting body that has a light weight, a preferable conductivity, and good chemical and thermal resistance, can maintain dimensional accuracy despite its thin and long shape, and is not oxidized nor deteriorated in the air to maintain a stable quality. It is a second object of this invention to provide an organic photosensitive body with a cylindrical supporting body that has an adequate and uniform surface roughness. It is a third object of this invention to provide an organic photosensitive body with a cylindrical supporting body that has mechanical strength large enough to prevent deformation despite its thin and long shape. It is a fourth object of this

invention to provide an organic photosensitive body with a cylindrical supporting body to which an organic material layer can adhere sufficiently during coating and formation. It is the fifth object of this invention to provide an efficient manufacturing method of cylindrical supporting bodies, in particular, those with a small thickness and diameter and a large length, as described in the first, second, and third objects.

According to this invention, the first object is achieved by providing an organic photosensitive body wherein an organic photosensitive layer is provided on a cylindrical supporting body composed of a material of $10^{-4} \Omega \cdot \text{cm}$ or less in volume resistivity formed by blending a crosslinked-type PPS resin as a main component with a highly conductive carbon black of $10^{-1} \Omega \cdot \text{cm}$ or less in volume resistivity.

The second object is achieved by providing a cylindrical supporting body wherein the average particle diameter of a carbon black contained therein is 20 to 50 nm.

When a carbon black is added to the supporting body, a carbon black dispersing agent can be preferably added simultaneously to uniformly disperse the carbon black in the supporting body material. The dispersing agent may be a calcium carbonate or clay.

The third object can be achieved by providing a cylindrical supporting body containing glass fibers as a reinforcement.

As described above, the supporting body material is a crosslinked-type PPS resin to which a carbon black, a carbon black dispersing agent, and glass fibers are added; the amount of the crosslinked-type PPS resin should be at least 40 wt.% or more so that the resin can act favorably for the supporting body.

The fourth object can be achieved by irradiating the surface of the cylindrical supporting body with ultraviolet rays 180 to 255 nm in wavelength or inducing corona discharge thereon.

The fifth object can be achieved by injection-molding a material $10^{-4} \Omega \cdot \text{cm}$ in volume resistivity formed by blending a crosslinked-type polyphenylenesulfide resin as a main component with a highly conductive carbon black $10^{-1} \Omega \cdot \text{cm}$ or less, or the above material wherein the average particle diameter of the carbon black is 20 to 50 nm or to which glass fibers are added.

The metal mold for injection-molding is preferably heated within a range of 120 °C to 150 °C and molding material is preferably heated within a range of 280

°C to 330 °C. Filling of an injection-molding material is preferably completed in 0.05 to 2.5 seconds.

It is also preferable to use a mold wherein a core mold is finished to have a surface roughness of 1 μm or less at the maximum height R_{max} and a draft angle of 0.15° to 0.25° on one side; the inner surface of a cavity mold does not have a draft angle, is electroformed with a nickel alloy, finished to have a surface roughness of 1 μm or less at the maximum height R_{max} , and has inside of the end face that contacts a fixed mold a stage section via which a material is filled into a cavity using a side gate method; and the circumference of the cavity mold is sectioned into at least three at the end face of the fixed mold that contacts the cavity mold and a spring knock is provided in each section to ensure that when the mold is opened, the injection-molded product remains in the cavity mold due to the effect of the spring knock.

Table 1 shows the chemical resistance of both crosslinked-type and linear-type PPS resins evaluated in terms of changes in mass (%) after immersion in acetone, methylene chloride, and dichloroethane respectively for 24 hours using cylindrical molded products composed of the respective resins, and their thermal resistance evaluated in terms of changes in diametral and longitudinal dimensions (%) after heating at 120 °C for 48 hours.

Table 1

Properties	Linear-type PPS resin	Crosslinked-type PPS resin
Chemical resistance (changes in mass after immersion for 24 hours (%))		
acetone	+0.05	0
methylene chloride	+12.42	+0.13
dichloroethane	+3.40	0
Thermal resistance (changes in dimensions 48 hours after heating at 120°C (%))		
diametral direction	0.67	-0.01
longitudinal direction	-1.20	0

As is apparent from Table 1, the crosslinked-type PPS resin is superior to the linear-type PPS resin in terms of both chemical and thermal resistance. The

formation of a supporting body with a crosslinked-type PPS resin as a main component reduces swelling caused by the thermal deformation of the supporting body or a solution of coating liquid during the coating and formation of an organic material layer such as a photosensitive layer, also reduces the deformation of the supporting body, and provides practically sufficient dimensional accuracy even for an photosensitive body using a supporting body of a small thickness and diameter and a large length.

The addition of a highly conductive carbon black of $10^{-1} \Omega \cdot \text{cm}$ in volume resistivity, for example, highly conductive carbon black or a more highly conductive channel black into a material containing a crosslinked-type PPS resin as a main component in order to apply conductivity to the material, reduces to 20 wt.% or less the quantity of carbon black to be added to the supporting body to reduce its volume resistivity to $10^{-4} \Omega \cdot \text{cm}$ or less, and possibly keeps the viscosity of the supporting body material low enough to allow the supporting body to be injection-molded despite its small diameter and thickness and large length; for example, the melt flow rate (MFR) can be maintained within a range of 20g/10min. to 50g/10min. at 300 °C.

Of course, the carbon black is preferably dispersed uniformly in the supporting body material. To do this, a dispersing agent is desirably added to the material; applicable dispersing agents include a calcium carbonate and clay. Although the quantity of dispersing agent to be added depends on the quantity of carbon black to be added, it should be 10 to 30 wt.% of the supporting body material. Less than 10 wt.% of dispersing agent has no effects, while more than 30 wt.% of dispersing agent is not preferable due to its adverse effect on the conductivity of the material.

Although the surface roughness of the supporting body depends upon the surface roughness of the inner surface of the cavity mold of the metal mold, it is affected greatly by the particle size of the carbon black. A carbon black 20 to 50 nm in average particle diameter enables the surface roughness of the supporting body to be within a range of 0.5 to 1.2 μm at R_{max} .

The addition of glass fibers to the supporting body compensates for a decrease in mechanical strength caused by the addition of a carbon black, providing strength of $0.49 \times 10^8 \text{ N/m}^2$ or more required for a supporting body about 1 mm in thickness. The glass fiber preferably has a diameter of 20 μm and a length of 3 mm. Although the quantity of glass fibers to be added depends on the quantity of carbon black to be added, it should be 10 to 30 wt.% of the supporting body material. Less than 10 wt.% of glass fibers have no effects, while more than 30 wt.% of glass fibers are not preferable due to its adverse effect on the conductivity of the material and the surface roughness of

the supporting body.

As described above, the supporting body is a crosslinked-type PPS resin to which a carbon black, a carbon black dispersing agent, and glass fibers are added; provision of at least 40 wt.% or more of resin allows it to function effectively without losing its character.

A disadvantage of the PPS resin is its low adhesion. In the electronics- and automobile-related field in which PPS resins are used as engineering plastics, methods for irradiating the surface with ultraviolet rays or inducing corona discharge thereon to modify the surface to improve adhesion have been known (The Adhesion Society of Japan 31st Annual Convention (June, 1993): Improvement of PPS Adhesion; Journal of The Adhesion Society of Japan Vol. 29, No. 4 (1993): Improvement of Surfaces Using Ultraviolet Rays). However, it has been unknown whether or not these methods can be used effectively without degrading the functions of the supporting body if a crosslinked-type PPS resin is used as a functional material for the supporting material of photosensitive body. The inventors discovered that irradiation with ultraviolet rays of 180 to 255 nm in wavelength causes ozone to be generated from oxygen in the air due to ultraviolet energy to cut molecular chains on the utmost surface of the crosslinked-type PPS resin and to generate a -OH and a -COOH group due to the additional effect of moisture in the air to activate the surface, thereby substantially improve the wettability and adhesion of the surface. Corona discharge energy also causes ozone to be generated to produce effects similar to those in irradiation with ultraviolet rays.

The supporting body for a photosensitive body in accordance with this invention is made by injection-molding a material containing a crosslinked-type PPS resin as a main component to which a carbon black, a carbon black dispersing agent, and glass fibers are added. A supporting body with required shape and surface roughness can be manufactured accurately and efficiently by integrally forming a metal mold with an adequate structure under adequate molding conditions. This obviates the need of individual surface-roughness-machining and other machining processes required when an aluminum alloy is used to manufacture a supporting body. Heating the metal mold within a range of 120 to 150 °C during injection-molding; heating

the molding material within a range of 280 to 330 °C; applying sufficient injection pressure; and completing filling of a material in 0.05 to 2.5 seconds allow the material filling to be completed before the resin starts to be solidified within the cavity (material-filled section) to provide a well-shaped supporting body, and cause the resin to be crystallized sufficiently to enable the crosslinked-type PPS resin to function effectively.

Next, the effects of the metal mold used to manufacture the supporting body in accordance with this invention are described with reference to the drawings. Figures 3 through 5 are partially sectional views describing an embodiment of the metal mold in accordance with this invention. Figure 3 shows the closing condition in which the end face of a cavity mold 6 contacts firmly to the end face of a fixed mold 8, wherein reference numeral 7 designates a core mold and reference numeral 9 is a cavity into which a molding material is filled and molded. Figure 4 shows the opening condition in which the cavity mold 6 and the fixed mold 8 are separated after molding. Reference numeral 14 designates a molded product. The core mold 7 is fitted into the fixed mold 8 and fixed thereto. Figure 5 is a partially enlarged sectional view of a spring knock 11 and its periphery in Figure 3. Reference numeral 12 designates a spring, while reference numeral 13 designates a knockout pin.

A stage section 10 is formed inside of the end face of the cavity mold 6 that contacts the fixed mold 8. "h" in the stage section 10 shown in Figure 5 should preferably be 1 to 3 mm and "w" should be 2 to 5 mm. In the closing condition shown in Figure 3, when a molding material is filled into the cavity 9 via this stage section 10 using side gate method, the material fills the stage section 10 and then the thin cylinder-like cavity 9, allowing the cavity 9 to be filled quickly, and circumferentially uniformly up to its tip of cavity 9 without producing defects such as a weld line. A gas vent is preferably provided at the tip of the cavity 9, and if desired, vacuum venting is preferably enabled to fill a molding material quickly in 0.05 to 2.5 seconds. The inside of the cavity mold 6 is electroformed with a nickel alloy to allow the molded product to be molded and released properly, and its surface roughness is finished to be 1 μm or less at the maximum height R_{max} . The use of the cavity mold 6 with such surface conditions to fill and solidify a material in the cavity 9 at a sufficient injection pressure results in an injection-molded supporting body whose surface roughness is 1 μm or less at the maximum height R_{max} .

However, a uniform outer diameter is required for a photosensitive body, and a draft angle must not be applied in the outer diameter of a molded product. Such molded products, in particular, those with a small thickness are difficult to release from the cavity mold 6 without damaging their surface. The surface of the core mold 7 is thus finished to be smooth so that its surface roughness is 1 μm or less at the maximum height R_{max} . A draft angle within a range of 0.15° to 0.25° is provided on one side. The fixed mold 8 is provided with at least three spring knocks 11 comprising knockout pin 13 and a spring 12 at its end face opposite to the circumference of the end face of the cavity mold 6. This configuration causes the spring 12 compressed during closing as shown in Figure 5 to extend upon opening, thereby causing the tip of the knockout pin 13 to protrude from the end face of the fixed mold 8 as shown in Figure 4. The

length by which the tip of the knockout pin protrudes from the end face is "m" shown in Figure 5. Thus, when the fixed mold 8 is separated from the cavity mold 6 and opened after molding, the tip of the knockout pin 13 continues pushing the end faces of the cavity mold 6 and molded product until the two molds 6 and 8 are separated by the distance equal to length "m". The cavity mold 6 and the molded product 14 thus move integrally, and, after opening, the molded product 14 is detached from the core mold 7 and remains fixed to the cavity mold 6, as shown in Figure 4. Since the core mold 7 has a draft angle and its surface is finished to be smooth, the core mold 7 can be pulled out smoothly from the molded product 14. Once the core mold has been pulled out, the molded product 14 contracts diametrically, allowing the molded product 14 to be, for example, knocked out from the cavity mold 6 without damaging its surface. If the draft angle of the core mold 7 is less than 0.15° on one side, the core mold is difficult to remove; if the draft angle is more than 0.25° on one side, the thickness of the thinner end of the supporting body, which is a molded product, will be too small to carry out molding if the supporting body is about 3 mm or less in thickness. For example, when the draft angle is 0.25° on one side and a supporting body of 30 mm in outer diameter, 300 mm in length, and 1.5 to 3 mm in thickness of the thicker end is used, the thickness of the thinner end will be 0.3 to 0.6 mm if the thickness of the thicker end is 1.5 to 3 mm, making molding very difficult. The draft angle should thus be within a range of 0.15° to 0.25° on one side.

Figure 6 is a perspective view illustrating a molded product removed from the metal mold, wherein a ring-like projection 15 is formed at one end of the cylindrical supporting body 1 so as to correspond to the stage section 10 of the cavity mold 6. Reference numeral 16 designates a side gate.

Figure 1 is a typical cross-sectional view of an embodiment of supporting body for a photosensitive body in accordance with this invention. Figure 1(a) is a longitudinal section of a supporting body 1, and Figure 1(b) is a cross-sectional view taken along line X-X of Figure 1(a). Figure 2 is a typical cross-sectional view illustrating the configuration of the layers of an embodiment of photosensitive body. In this figure, a photosensitive layer 3 is formed by laminating via an under-layer 2 an electric charge generation layer 4 and an electric charge transport layer 5 in this order on the supporting body 1 shown in Figure 1. The under-layer 2 is not always necessary but is provided when needed.

Example 1

Using materials 1-1 to 1-4 of the compositions shown in Table 2 and a metal mold shown in Figures 3 to 5, supporting bodies 1 to 3 were formed by injection-molding under the same molding conditions, while a supporting body

4 was formed by injection-molding at a different metal mold temperature using a material 1-4 composed of a linear-type PPS resin. The injection-molding was carried out using a draft angle on one side to obtain supporting bodies with an outer diameter of 30 mm, a length of 260.5 mm, and an inner diameter of 28.5 mm for the thinner end and 26.5 mm for the thicker end.

Table 2

Raw material	Raw material brand	Compounding ratio (wt.%)			
		Material 1-1	Material 1-2	Material 1-3	Material 1-4
Crosslinked-type PPS resin	Toray PPS M2900 (MFR: 600)	60	-	-	-
	Toray PPS M3910 (MFR: 2000)	-	50	50	-
Linear-type PPS resin		-	-	-	50
Carbon black	Cabot Furnace Carbon XC12 (particle size: 30 nm)	15	-	-	-
	Cabot Furnace Carbon BP-480 (particle size: 30 nm)	-	20	10	20
Clay	Tsuchiya Kaoline SATINTONES	10	15	25	15
Glass fibres	Nihon Sheet Glass RES 03-TP76 (diameter: about 20 μ m, length: about 3mm)	15	15	15	15

Table 3

Supporting body No.	1-1	1-2	1-3	1-4
Supporting body material	Material 1-1	Material 1-2	Material 1-3	Material 1-4
Cylinder temperature (°C)	280	Same as the values on the left	Same as the values on the left	280
Rear	290			290
Middle	300			300
front				
Nozzle temperature (°C)	310			300
Metal mold temperature (°C)	150			120
Injection pressure	1.62			1.62

($\times 10^8$ N/m ²)				
Filling time (sec)	0.1			0.1
Cooling time (sec)	30			30

The following photosensitive layers were formed on these supporting bodies under the same conditions to produce photosensitive bodies. That is, a coating liquid with 5 parts weight alcohol-soluble polyamide resin (manufactured by Toray Co., Ltd.; Amilan CM 8000) solved in 95 parts weight methanol was coated on a supporting body by a dipping method and then dried at 120 °C for 15 minutes to form an under-layer 0.5 μ m in thickness. A coating liquid formed by blending and dispersing 10 parts weight X-type non-metal phthalocyanine (manufactured by Dainippon Ink and Chemicals Inc.; FASTGEN BLUE 8120), 10 parts weight vinyl chloride resin (manufactured by Nippon Zeon Co., Ltd.; MR-110), 686 parts weight dichloromethane and 294 parts weight 1, 2 -dichloroethane in a mixer for one hour and further dispersing the mixture by a supersonic dispersing machine for 30 minutes, was coated on the under-layer by a dipping method and then 0.5 μ m in film thickness. A coating liquid consisting of 100 parts weight hydrazone compound (manufactured by Fuji Electric Co., Ltd.) shown in structural formula (I), 100 parts weight polycarbonate resin (manufactured by Mitsubishi Gas Chemical Co., Ltd.; lupilon PCZ), and 800 parts weight dichloromethane was coated on the electric charge generation layer by a dipping method and then dried at 90 °C for one hour to form a electric charge transport layer of 20 μ m in thickness, thereby producing a photosensitive body.

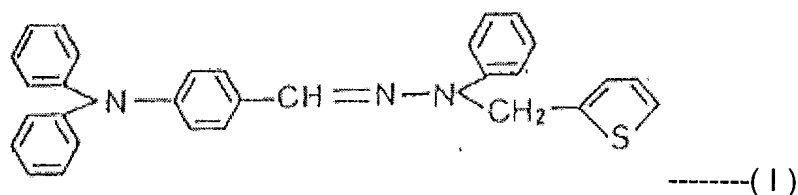


Table 4 shows the MFR at 300 °C, volume resistivity, injection-moldability, mechanical strength, and chemical resistance (evaluated in terms of changes in mass during immersion in a methylene chloride for two hours) of the supporting body material, and the surface roughness (at the maximum height R_{max}), outer diameter accuracy, and change in dimensions measured after heating at 120 °C for 48 hours each of supporting body, and the potential retaining rate V_{ks} measured after 5 seconds after charging in a dark place, residual potential V_r measured after irradiation of 10 μ J/cm² with

monochromatic light 780 nm in wavelength, and the printing characteristics evaluated by installing the photosensitive body in a commercially available semiconductor laser printer of each photosensitive body.

Table 4

Sensitive body No.	1-1	1-2	1-3	1-4
Supporting body No.	1-1	1-2	1-3	1-4
MFR (g/10min)	30	40	30	40
Volume resistivity ($\Omega\cdot\text{cm}$)	2×10^3	3×10^2	10^6	3×10^2
Injection moldability	good	good	bad	nearly good
Mechanical strength ($\times 10^8 \text{ N/m}^2$)	0.68	0.68	0.74	0.78
Chemical resistance (%)	+0.5	+0.1	+0.1	+12.4
Surface roughness R_{max} (μm)	0.9	0.8	0.8	0.8
Outer diameter accuracy (mm)	0.05	0.03	0.03	0.05
Dimensional change rate (%)	0	0	0	-0.7
Vks (%)	90	92	93	92
Vr (V)	31	34	60	35
Printing characteristics	good	good	bad	nearly good

As can be seen from Table 4, the supporting body 1-4 using the material 1-4 composed of a linear-type PPS resin as a main component has inferior chemical resistance than that of the supporting bodies 1-1, 1-2, and 1-3 using the materials 1-1, 1-2, and 1-3 respectively composed of a crosslinked-type PPS resin as a main component, while it has a larger dimensional change rate than that of the supporting bodies 1-1, 1-2, and 1-3. In addition, the photosensitive body 1-3 using the supporting body 1-3 with a high volume resistivity of $10^5 \Omega\cdot\text{cm}$ has bad printing characteristics. It is obvious that supporting bodies consisting of a material comprising a crosslinked-type PPS resin as a main component and having volume resistivity of $10^4 \Omega\cdot\text{cm}$ or less can produce good effects.

Example 2

An ultraviolet ray irradiation device (SUV200NS) manufactured by Sen Engineering Co., Ltd. was used to irradiate the surface of the supporting body 1-1 described in Example 1 with ultraviolet rays of 184.9 and 253.7 nm in wavelength from a 200 W low pressure mercury lamp, keeping a distance of 20 mm from the supporting body. The supporting body irradiated for 10 seconds was referred to as 2-1, while the supporting body irradiated for 20 seconds was referred to as 2-2.

In addition, corona discharge was induced on the surface of the supporting body 1-1 while it was being rotated (discharge voltage: about 10 kV; gap between a discharge electrode and the supporting body: 2 to 3 mm; and discharge time: 30 seconds). This supporting body was referred to as 2-3.

For comparison, the supporting body 1-1 on which no corona discharge treatment was applied was referred to as 2-4.

The contact angle of the surface of these supporting bodies with respect to pure water was determined, and cross-cut adhesion tests (JIS K5400 8.5.1) were conducted to evaluate adhesion.

Each supporting body was then used to produce photosensitive bodies 2-1, 2-2, 2-3, and 2-4 as in Example 1. The photosensitive bodies were then installed in a commercially available semiconductor laser printer to evaluate their continuous printing life, that is, when their photosensitive layer starts being separated from the supporting body.

Table 5 shows the results.

Table 5

Photosensitive body No.	2-1	2-2	2-3	2-4
Supporting body No.	2-1	2-2	2-3	2-4
Surface treatment				
ultraviolet ray irradiation (second)	10	20	-	-
corona discharge (second)	-	-	30	-
Contact angle (degree)	32	0	0	78
Cross-cut adhesion test (separations/100)	85/100	0/100	0/100	100/100
Continuous printing life (times)	50,000	100,000	100,000	5,000

Table 5 clearly shows that the photosensitive bodies 2-1 and 2-2 using the supporting bodies 2-1 and 2-2 irradiated with ultraviolet rays and the photosensitive body 2-3 using the supporting body 2-3 on which corona discharge was induced were better in adhesion and continuous printing life than the photosensitive body 2-4 using the supporting body 2-4 on which no treatment was applied. For irradiation with ultraviolet rays from a 200 W low pressure mercury lamp, the results were particularly good when the irradiation time was 20 seconds. It can thus be estimated that the irradiation time is preferably 15 to 25 seconds.

Example 3

The material 1-3 in Table 2 and the metal mold in Figures 3 to 5 were used to carry out injection-molding at various metal mold temperatures as shown in

Table 6 to produce supporting bodies 3-1, 3-2, and 3-3. The nozzle temperature was somewhat changed along with the variation of the metal mold temperature. For the supporting material 3-3, an increase in metal mold temperature results in a shorter material-filling time. Among the supporting bodies formed, the supporting body 3-3 was inadequate for practical use due to many burrs. The supporting bodies 3-1 and 3-2 were then used to produce photosensitive bodies 3-1 and 3-2 as in Example 1 to determine their potential retaining rate V_{ks} , residual potential V_r and printing characteristics. Table 7 shows the results.

Table 6

Supporting No.	3-1	3-2	3-3
Cylinder temperature(°C)	280	280	280
Rear	290	290	290
Middle	300	300	300
front			
Nozzle temperature(°C)	310	300	319
Metal mold temperature (°C)	150	100	170
Injection pressure			
($\times 10^8$ N/m ²)	1.62	1.62	1.57
Filling time(sec)	0.1	1.0	0.04
Cooling time(sec)	30	30	30

Table 7

Photosensitive body No.	3-1	3-2
V_{ks} (%)	92	93
V_r (V)	34	55
Printing characteristics	good	bad

As is apparent from Tables 6 and 7, good supporting bodies cannot be obtained unless adequate injection-molding conditions are set even if the same material is used. Good results can be obtained when the metal mold temperature is 150 °C, while printing is bad when this temperature is 100 °C and many burrs are generated when this temperature is 170 °C. The metal mold temperatures is preferably higher than 100 °C and lower than 170 °C, and, more preferably, within a range of about 120 °C to about 160 °C.

With the above configuration, this invention has the following advantages:

The use of a material $10^4 \Omega\cdot\text{cm}$ in volume resistivity formed by blending a crosslinked-type PPS resin as a main component with a highly conductive carbon black $10^{-1} \Omega\cdot\text{cm}$ or less serves to provide an organic photosensitive body with a cylindrical supporting body that has a light weight, preferable conductivity, and good chemical and thermal resistance, can effectively maintain dimensional accuracy despite its thin and long shape, and is not deteriorated by oxidation in the air, thereby eliminating the need of a special treatment for surface stabilization.

Blending with a carbon black of 20 to 50 nm in average particle diameter serves to provide an organic photosensitive body with a cylindrical supporting body that has a uniform surface roughness within a range of 0.5 to 1.2 μm at R_{max} . When the carbon black is added to the supporting body, a carbon black dispersing agent can preferably be added together to uniformly add the carbon black, thereby making the supporting body homogeneous and the surface roughness uniform.

Moreover, the addition of glass fibers serves to provide an organic photosensitive body with a cylindrical supporting body that has a high mechanical strength and is difficult to deform despite its thin and long shape. Glass fibers of about 20 μm in diameter and about 3 mm in length are preferable due to the lack of adverse effects on the surface roughness of the supporting body. The addition of various materials does not affect the favorable characteristics of the supporting body as long as at least 40 wt.% or more of the supporting body material is composed of a crosslinked-type PPS resin.

Irradiating the surface of the supporting body with ultraviolet rays 180 to 255 nm in wavelength or inducing corona discharge thereon serves to provide a long life organic photosensitive body with a cylindrical supporting body that has better adhesion and on which an organic material layer can be formed stably.

The above cylindrical supporting body can be manufactured efficiently by injection-molding a material $10^4 \Omega\cdot\text{cm}$ in volume resistivity formed by blending a crosslinked-type PPS resin as a main component with a highly conductive carbon black $10^{-1} \Omega\cdot\text{cm}$ or less in volume resistivity, or the above material wherein the average particle diameter of the carbon black is 20 to 50 nm or to which glass fibers are added.

The above molding material can be molded effectively and the

crosslinked-type PPS resin is crystallized sufficiently to act favorably for the supporting body when the mold temperature is within a range of 120 °C to 150 °C and the molding material temperature is within a range of 280 °C to 330 °C.

Completion of filling of a material in 0.05 to 2.5 seconds preferably serves to form efficiently a thin and long cylindrical supporting body. In the metal mold used, the core mold fitted into the fixed mold is finished to have a surface roughness of 1 μm or less at the maximum height R_{max} and a draft angle of 0.15° to 0.25° on one side; the inner surface of the cavity mold does not have a draft angle; is electroformed with a nickel alloy; is finished to have a surface roughness of 1 μm or less at the maximum height R_{max} ; and has inside its end face that contacts the fixed mold a stage section via which a material is filled using a side gate method; the fixed mold is provided with at least three spring knocks at its end face opposite to the end face of the cavity mold to ensure that when the mold is opened after molding, the injection-molded product remains in the cavity mold due to the effect of the spring knock. The use of a metal mold of this configuration serves to easily reduce the molding material filling time down to 0.05-2.5 seconds, allows the molding material to be uniformly filled circumferentially up to the tip of the cavity before the material starts to be solidified, and enables thin and long supporting bodies to be formed adequately. Supporting bodies of 1 μm in surface roughness at the maximum height R_{max} can also be obtained corresponding to the roughness of the inner surface of the cavity mold. When the mold is opened after injection-molding, the core mold can be pulled out smoothly from the molded product due to its draft angle, which can then be, for example, knocked out from the cavity mold without damaging its surface.

Brief Description of the Drawings

Figure 1 is a typical sectional view of an embodiment of a supporting body in accordance with this invention; Figure 1(a) is a longitudinal section, while Figure 1(b) is a cross-sectional view taken along line X-X of Figure 1(a).

Figure 2 is a typical sectional view of an embodiment of a photosensitive body in accordance with this invention.

Figure 3 is a partially sectional view of the closing condition describing an embodiment of a metal mold in accordance with this invention.

Figure 4 is a partially sectional view of the opening condition describing an embodiment of a metal mold in accordance with this invention.

Figure 5 is a partially enlarged sectional view of a spring knock section and its

periphery in Figure 3.

Figure 6 is a perspective view illustrating a molded product removed from the metal mold.

Description of Symbols:

- 1 Supporting body
- 2 Under-layer
- 3 Photosensitive layer
- 4 Electric charge generation layer
- 5 Electric charge transport layer
- 6 Cavity mold
- 7 Core mold
- 8 Fixed mold
- 9 Cavity
- 10 Stage section
- 11 Spring knock
- 12 Spring
- 13 Knockout pin
- 14 Molded product
- 15 Ring-like projection
- 16 Side gate

Figure 1

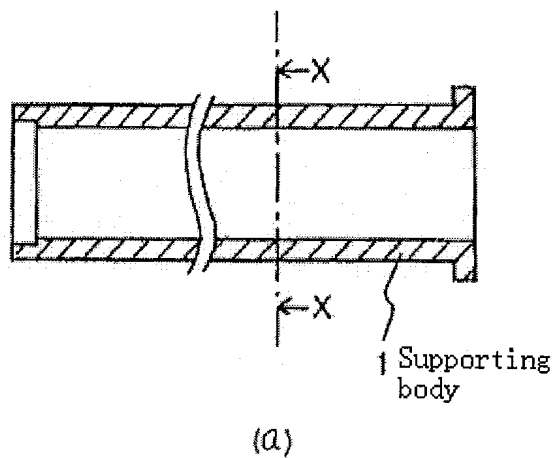


Figure 2

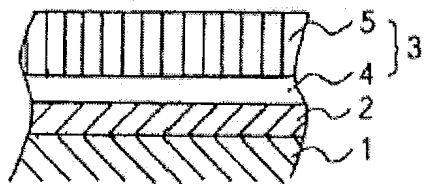


Figure 3

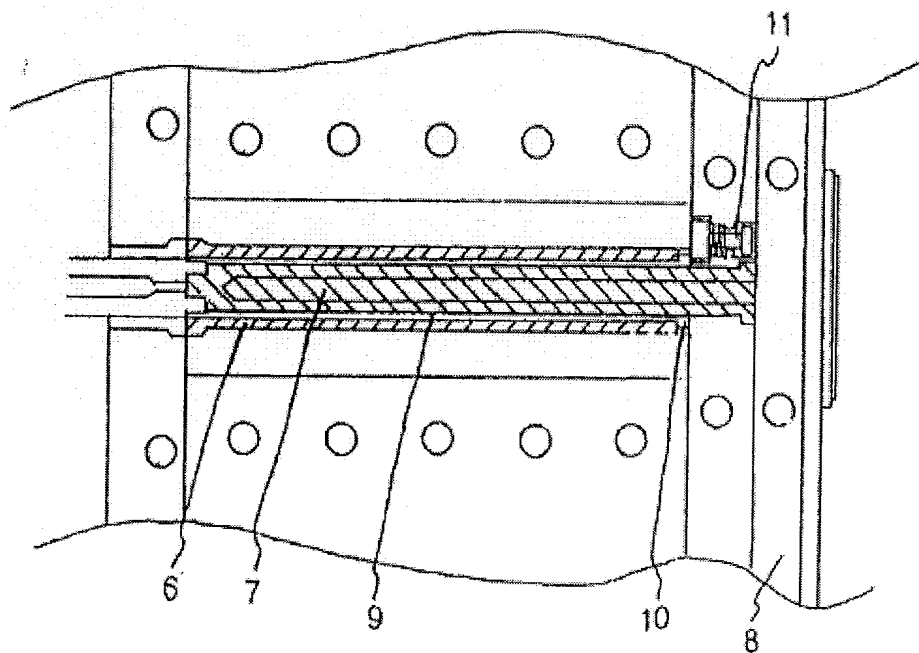


Figure 4

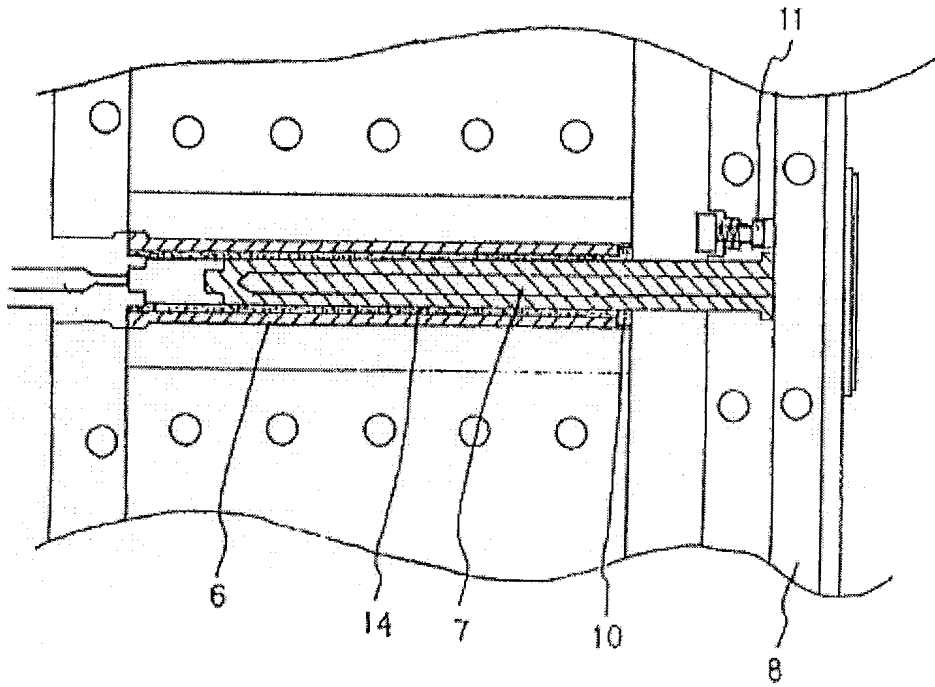


Figure 5

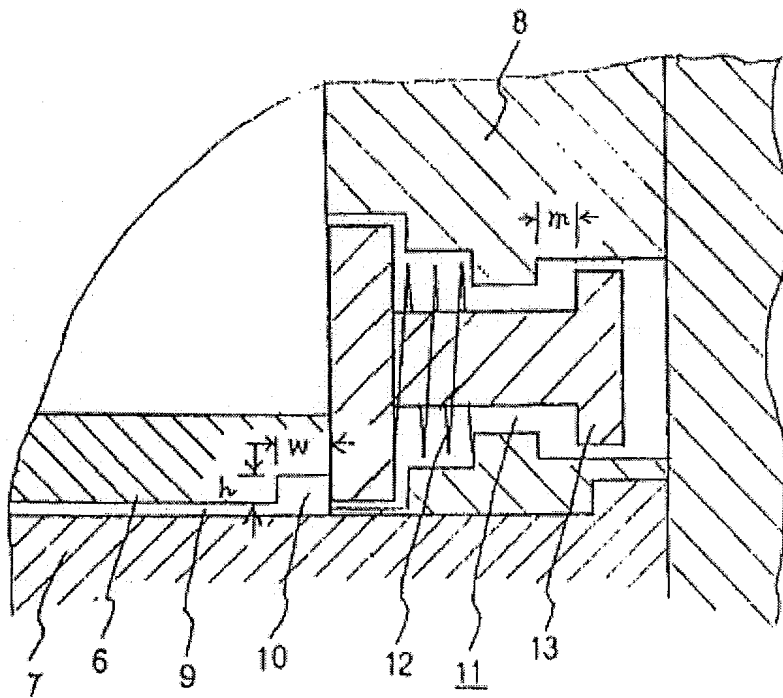


Figure 6

